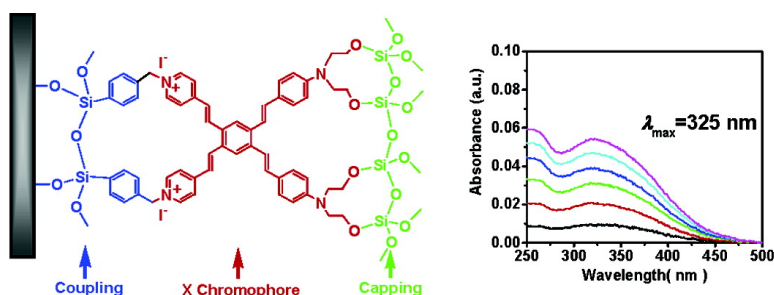


Self-Assembled Electrooptic Thin Films with Remarkably Blue-Shifted Optical Absorption Based on an X-Shaped Chromophore

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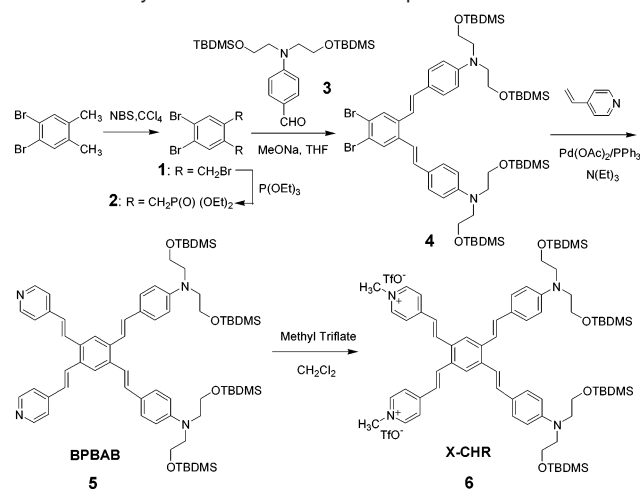
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Molecule-based electrooptic (EO) materials are of great current interest for optoelectronic and photonic technologies such as high-speed optical communications, integrated optics, and optical data processing and storage.¹ Crucial synthetic challenges for large bulk EO response are that individual chromophore components have large molecular hyperpolarizabilities (β) and that they be arranged in a noncentrosymmetric architecture. Large- β EO chromophores are typically devised according to similar design principles: one-dimensional (1D) planar conjugated π systems end-capped with donor and acceptor (D, A) moieties. Chromophores of this type usually exhibit a single, intense, low-lying longitudinal charge-transfer (CT) excitation, the energy and transition dipole of which determine the principal β tensor within a two-level model.² Considerable, elegant efforts have striven to increase β by optimizing D/A strengths and/or the conjugation pathways of such one-dimensional (1D) chromophores.³ However, intrinsic to this approach is the challenge of optimizing the nonlinearity–transparency tradeoff in which increases in β for such chromophores are almost invariably accompanied by bathochromic shifts of the optical maximum. Furthermore, molecules with extended π systems and low-lying excited states are frequently subject to chemical and thermal instability.⁴ Alternative design strategies at the molecular level are therefore desirable. To this end, nontraditional NLO chromophores with multiple donor–acceptor substitution have attracted recent attention, ranging from dipolar “X-shaped”⁵ and “A-shaped”⁶ to octopolar molecules.⁷ Multiple D/A substitution affords two-dimensional (2D) β tensor character in which off-diagonal components become significant, offering among other attractions, possible relaxation of nonlinearity–transparency tradeoffs and improved phase-matching via the larger off-diagonal components.⁸ However, few experimental studies of dipolar 2D EO chromophores have been reported to date, with most molecules exhibiting modest hyperpolarizabilities due to short conjugation lengths, and only a few incorporated in LB or poled polymer thin films.^{5b,c,8}

We report here the synthesis and incorporation in intrinsically acentric EO-active thin films of a novel type of “X-shaped” 2D chromophore containing a central aromatic core fused to extended conjugated D/A tetrasubstitution. The optical transition dipoles couple in such a manner as to drastically blue-shift λ_{\max} while maintaining a very large β response.⁹ This chromophore was specifically designed for a covalent layer-by-layer siloxane self-assembly (SA) approach¹⁰ to afford polar, robust, and structurally regular thin films. To our knowledge, this is the first example of blue-shifted chromophore incorporation in such a SA approach. Chromophore precursor 1,2-bis-((*E*)-2-pyridin-4-yl-vinyl)-4,5-bis-((*E*)-2-[*p*-*N,N*-bis(2-*tert*-butyldimethylsiloxyethyl)amino-phenyl]-ethenyl)benzene (**BPBAB**) was synthesized via a sequence of Wittig–Horner and Heck coupling reactions (Scheme 1). The dicationic methylpyridinium X chromophore (**X-CHR**) was next obtained via MeOTf alkylation of **BPBAB**. All new compounds

Scheme 1. Synthetic Route to X Chromophore



were characterized by conventional analytical/spectroscopic techniques.¹¹ Thermal analysis data show that both **BPBAB** and **X-CHR** have high thermal stability ($T_d \approx 340$ °C for **BPBAB** and $T_d \approx 280$ °C for **X-CHR**).

The **X-CHR** optical spectrum¹¹ in CH_2Cl_2 solution consists of an intense band centered at 357 nm ($\epsilon = 12000 \text{ L mol}^{-1} \text{ cm}^{-1}$), involving $\pi \rightarrow \pi^*$ CT and a less intense, broad band at 440–700 nm, responsible for the red color, and ascribed to aggregation as supported by concentration-dependent optical absorption spectra (5×10^{-7} to 3×10^{-8} M), which reveal an increase of the 357 nm CT band and diminution of the long- λ band upon dilution.¹² This strong tendency for aggregation is also evident in concentration-dependent NMR experiments.¹¹ The blue-shifted X chromophore HOMO–LUMO CT excitation can be understood in terms of the excitonic coupling of transition dipoles,^{9,13} leading to a first excited state composed of a pair of excitonic states. The upper excitonic state is optically allowed, and optical transitions from the ground-state populate the upper excitonic state, resulting in the spectral blue shift. In the X chromophore, *intramolecular* coupling of transition dipoles in two dimensions is sufficiently strong as to afford a dramatically blue-shifted optical maximum.

Layer-by-layer self-assembled X chromophore-derived thin films were fabricated on a variety of substrates (glass, quartz, silicon) via an iterative three-layer process (Scheme 2): (i) self-limited chemisorption of 4- $\text{Cl}_2\text{SiC}_6\text{H}_4\text{CH}_2\text{I}$ onto a hydrophilic substrate surface, (ii) SA of chromophore precursor **BPBAB** onto the benzyl halide-functionalized substrate via quaternization, and (iii) $\text{Cl}_3\text{SiOSi}(\text{Cl}_2)\text{OSiCl}_3$ capping to planarize/cross-link the polar structure and regenerate an active surface for subsequent layer deposition.¹¹ Specular X-ray reflectivity data indicate a narrow distribution of layer thicknesses and a linear dependence of film thickness on the number of layers, from which an average interlayer spacing of 40.6 Å can be deduced.¹¹ The resulting films exhibit λ_{\max} at the

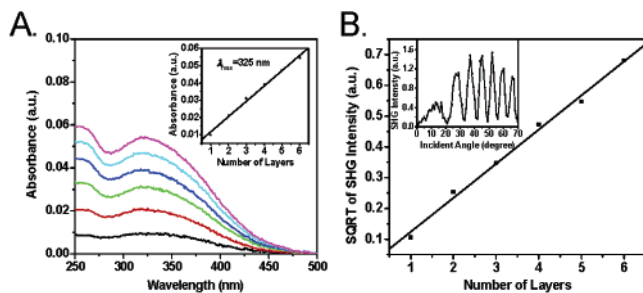
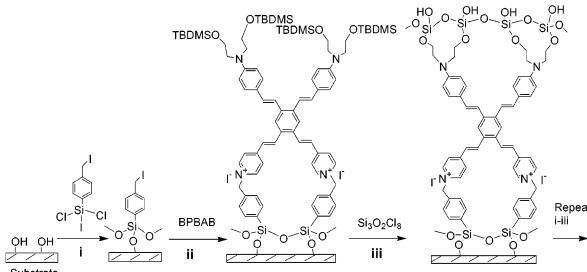


Figure 1. (A) Optical absorption spectra of X-chromophore SA films grown on fused quartz. (Inset) Optical absorbance of films at $\lambda_{\text{max}} = 325$ nm as a function of the number of layers. (B) Square-root of film 532 nm SHG response ($I^{2\omega}$, arbitrary units) as a function of the number of layers. (SHG) SHG response as a function of fundamental beam incident angle from a float glass slide having a film on either side.

Scheme 2. Self-Assembly of the X Chromophore



remarkably short wavelength of 325 nm (Figure 1A). The further blue-shifting of the film λ_{max} vs solution is consistent with *intermolecular* dipole–dipole coupling in the closely packed chromophore layers, where strong π – π interactions are possible.^{13b,14} The linear dependence of the 325 nm absorbance on the number of layers indicates that essentially equal quantities of equivalently oriented chromophore molecules are deposited in forming each layer. Polarized transmission second harmonic generation (SHG) measurements at $\lambda_0 = 1064$ nm yield angle-dependent interference patterns for glass substrates coated on both sides (Figure 1B inset) that demonstrate essentially identical film quality and uniformity are achieved on both sides of the substrates. The quadratic dependence of the 532 nm output intensity ($I^{2\omega}$) on film thickness (Figure 1B) further demonstrates polar microstructure preservation as layer-by-layer assembly progresses. The films exhibit large second-order *nonresonant* macroscopic NLO responses $\chi_{33}^{(2)} \approx 232$ pm/V at 1064 nm (obtained by calibration vs quartz), translating to an estimated EO coefficient $r_{33} \approx 43$ pm/V at 1550 nm.¹⁵

In summary, an “X-shaped” 2D EO chromophore with extended orthogonal conjugation was designed and synthesized. Self-assembled thin films of this chromophore were fabricated via a layer-by-layer chemisorptive siloxane-based approach. The chromophoric film exhibits a dramatically blue-shifted optical maximum (325 nm) while maintaining a large EO response ($\chi_{33}^{(2)} \approx 232$ pm/V at 1064 nm; $r_{33} \approx 43$ pm/V at 1550 nm).

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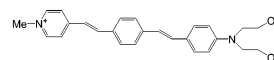
Supporting Information Available: Experimental details regarding chromophore synthesis, SA film fabrication, and characterizations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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$$r_{33} = \frac{2}{n^4} \frac{(3\omega_0^2 - \omega^2)(\omega_0^2 - \omega'^2)(\omega_0^2 - 4\omega'^2)}{3\omega_0^2(\omega_0^2 - \omega^2)^2} \chi_{33}^{(2)}$$

where ω , ω' are EO and SHG fundamental frequencies, respectively (i.e., 1550 and 1064 nm, respectively), ω_0 is the first resonance frequency (corresponding to λ_{max}), and n is the refractive index.

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